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THE EFFECT OF PYROLYSIS CONDITIONS ON BIOCHAR STABILITY AS DETERMINED BY THREE METHODS

Running Title - Crombie et al.: Assessing biochar stability

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Primary Research Article

Abstract

Biochar is the porous, carbonaceous material produced by thermo-chemical treatment of organic materials in an oxygen-limited environment. In general, most biochar can be considered resistant to chemical and biological decomposition, and therefore suitable for carbon (C) sequestration. However, to assess the C sequestration potential of different types of biochar, a reliable determination of their stability is needed. Several techniques for assessing biochar stability have been proposed, e.g. proximate analysis, oxygen (O): C ratio and hydrogen (H): C ratio, however, none of them are yet widely recognised nor validated for this purpose. Biochar produced from three feedstocks (Pine, Rice husk and Wheat straw) at four temperatures (350, 450, 550, 650°C) and two heating rates (5 and 100°C/min) was analysed using three methods of stability determination: proximate analysis, ultimate analysis and a new analytical tool developed at the UK Biochar Research Centre known as the Edinburgh accelerated aging tool (Edinburgh stability tool). As expected, increased pyrolysis temperatures resulted in higher fractions of stable C and total C due to an increased release of volatiles. Data from the Edinburgh stability tool was compared with those obtained by the other methods, i.e. fixed C, volatile matter, O:C and H:C ratio, to investigate potential relationships between them. Results of this comparison showed that there was a strong correlation ($R > 0.79$) between the stable C determined by the Edinburgh stability tool and fixed C, volatile matter and O:C, however H:C showed a weaker correlation ($R = 0.65$). An understanding of the influence of feedstock and production conditions on the long term stability of biochar is pivotal for its function as a C mitigation measure, as production and use of unstable biochar would result in a relatively rapid return of C into the atmosphere, thus potentially intensifying climate change rather than alleviating it.

Introduction

Biochar is the C-rich solid produced by thermo-chemical conversion (pyrolysis) of biomass in an oxygen depleted environment for the purpose of soil amendment. Biomass pyrolysis diverts C away from the dynamic atmosphere–biosphere pool and into a far more stable pool decomposing at a much slower rate than its parent feedstock (Preston & Schmidt 2006; Liang *et al.* 2008; Spokas 2010), avoiding the complete return to the air of CO₂ from natural decay or burning. Producing biochar and incorporating it into soil for the purpose of soil improvement is thus one proposed method to increase long term storage of C in the biosphere (Shackley *et al.* 2009; Sohi *et al.* 2010). As a relatively complex proposition that concerns energy production as well as C sequestration and soil management, it is the subject of increasing multi-disciplinary research.

It is known that the physiochemical properties of biochar depend on the starting organic material, the carbonization system used to make it and selected production parameters (Enders *et al.* 2012). These properties then define the functional properties such as biochar soil stability which is essential to demonstrating the longevity of stored C and therefore establish an effective means for C abatement.

Biochar can be considered part of the black C continuum, a term used to describe the by-products of combustion that also includes – in order of increasing stability – charcoal, coal, soot and graphite (Masiello 2004; Baldock & Smernik 2002; Liang *et al.* 2008). Through the use of C-14 dating, black C has been found to be the oldest fraction of C in soils, with the most stable components displaying mean residence times of several thousand years (Lehmann *et al.* 2009; Liang *et al.* 2008; Preston & Schmidt 2006). The complexity and chemical heterogeneity of black C has made it difficult to establish a single method suited to assessing the potential stability of all materials in the continuum (Hammes *et al.* 2006) and hence, there is no globally-established method for determination of absolute stability for

black C or biochar. However, a number of methods for comparing the relative stability of different biochar materials have emerged. These include proximate analysis (ASTM D1762-84; Antal & Gronil 2003), O:C or H:C molar ratios (Spokas 2010; Enders *et al.* 2012; IBI Guidelines 2012), and chemical oxidation (Cross & Sohi 2012).

Proximate analysis has long been used to assess the quality of coal and charcoal fuels, defining moisture, “volatile matter”, “fixed C” and ash. Proximate analysis requires high temperatures (900°C for determination of volatile matter and 750°C for ash determination) for extended periods of time, this has practical drawbacks and can lead to an inflated estimate of fixed C by underestimation of ash content (Masiello 2004; Downie *et al.* 2009; Enders *et al.* 2012). Furthermore, proximate analysis relies on thermal decomposition for calculation of products, which does not provide an analogue for the degradative (primarily oxidative) processes that exist in soil.

Pyrolysis favours the elimination of H and O over C, such that extending pyrolysis reactions results in a solid residue (char) of progressively higher C concentration. The utility of elemental ratios, provided by ultimate analysis, as indicators of biochar stability has been extensively researched (Kuhlbusch 1995; Hedges *et al.* 2000; Masiello 2004; Spokas 2010; IBI Guidelines 2012; Schmidt *et al.* 2012). The O:C ratios assigned to materials encompassed by the black C continuum showed a systematic increase from 0 for graphite to >0.6 for material not considered to be black C. For aged biochar samples, changes in O:C ratio at the surface indicates the extent to which they have been oxidised by their environment (Cheng *et al.* 2006). For newly produced samples, O:C indicates the progression of deoxygenation which can serve as a proxy for the extent of charring. Correlation of O:C with the mean residence time of various biochar samples in soil, extrapolated from various short-term incubation experiments confirmed a general, inverse relationship between this ratio and biochar stability (Spokas 2010). This work proposed that biochar displaying an O:C ratio

>0.6 would be closer to biomass composition than to graphite and would have a mean residence time <100 years. Conversely, material with an O:C ratio in the range 0.2–0.6 would be expected to have mean residence time of 100–1000 years. To avoid confounding analyses with non-black C species IBI guidelines for quantifying O:C ratio recommend the application of an acid treatment for the removal of carbonates and determination of organic C (IBI Guidelines 2012).

The ratio of H:C has also been proposed as an index of aromaticity and resistance of char to microbial and chemical degradation (Kuhlbusch 1995; Kuhlbusch & Crutzen 1995). As with O:C quantification, pre-treatment steps (acid and thermal treatment) can be applied to remove inorganic and organic C prior to total H and C determination. Kuhlbusch (1995) also described the use of a correction factor to exclude H bound to elements other than C, most likely silicate and therefore generating an H:C ratio only for the stable fraction of char. However, Enders *et al* (2012) showed that their results ranked poultry manure, based on H:C ratio, to have equal stability to woody samples which were found to be much more stable thus creating doubt over the suitability of H:C as a method of stability determination.

In order for the potential of biochar for C sequestration and agricultural benefit to be fully realised, it is necessary that the different functional characteristics of biochar such as stability can be rapidly assessed prior to deployment. The method put forward by Cross and Sohi (Cross & Sohi 2012) establishes an approach that directly quantifies stability by eliminating the less stable portion of material by oxidation. Controlled but fast addition of hydrogen peroxide (H₂O₂) is used as an analogue for the accumulated effect of oxidation over extended periods of time in soil. Biochar samples produced under subtly different conditions can be readily distinguished and the oxidation treatment tuned to mimic the loss of C occurring in charcoal over 50–200 yrs. in the environment (depending on ambient climate

conditions). The approach has potential to capture the effects of physical inaccessibility of biochar as a substrate, whereas thermal degradation may not.

A comprehensive comparison of the methods described is required for two reasons. Firstly, if methods are equivalent or can be correlated, the more practical and cost effective method may be promoted for future applications. Secondly, if results provided by different methods diverge, new insights into the nature of biochar may emerge, for example, the effect of contrasting abiotic conditions in the natural environment.

In the present study, a systematic set of biochar products was created from three contrasting feedstock materials using a single set of highly controlled small-scale pyrolysis equipment and defined temperature settings. The products were assessed using proximate analysis, elemental molar ratios and direct oxidation. The objective was to determine whether the different assessment methods provided a measure of the same characteristics and, where results showed different patterns, to consider the possible reasons.

Materials and Methods

Feedstock

The three types of biomass used in the pyrolysis experiments were: *Pinus spp* (mixed pine wood chips, PC), *Oryza sativa* (rice husk variety, RH) and *Triticum spp* (wheat straw, WS). Wood chips (ranging from $15 \times 5 \times 4$ mm to $100 \times 40 \times 15$ mm in dimension) were acquired from Stonelaws Farm in East Lothian, Scotland. Rice Husk (uniformly less than $5 \times 4 \times 1$ mm particle size) was obtained from Kameoka, Kyoto Prefecture, Japan. Wheat straw (primary fragments $10 \times 3 \times 1$ mm to $90 \times 5 \times 4$ mm) was purchased from StrawPellet Ltd., Rookery Farm, Lincolnshire, England. For pine wood chips and wheat straw the natural heterogeneity within bulk supply was minimised as far as possible by thoroughly mixing a volume sufficient for all experiments. The moisture content of each feedstock was determined gravimetrically by drying at 105°C for 24 hr. Results from ultimate and proximate analysis of the selected materials are shown in Table 1.

Table 1: Ultimate and proximate analysis for pine, rice husk and wheat straw feedstock used in experimental work.

| Feedstock | Fixed C % | Volatile Matter % | Ash % | Moisture % | C% | H% | N% | S% | O%* |
|-------------|--------------|----------------------|----------|---------------|------|-----|----|----|------|
| Pine | 21.6 | 73.2 | 2.0 | 3.3 | 49.5 | 5.9 | 0 | NM | 44.7 |
| Rice Husk | 15.0 | 59.4 | 21.3 | 4.3 | 37.9 | 4.9 | 0 | NM | 57.2 |
| Wheat Straw | 14.4 | 75.3 | 6.3 | 4.1 | 41.4 | 5.6 | 0 | NM | 53.1 |

NM, not measured

*, determined by difference

Equipment

Pyrolysis was conducted using the apparatus shown in Fig. 1 comprising a static bed reactor formed from a vertical 50 mm diameter quartz tube with sintered plate at the base allowing a sample bed depth of approx. 200 mm.

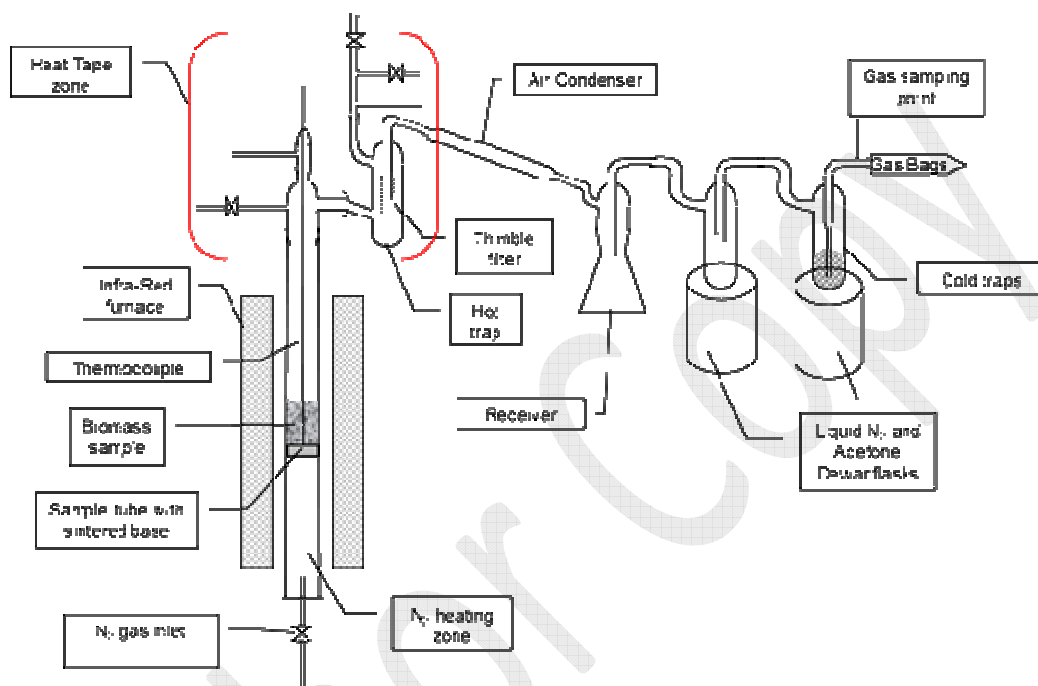


Fig. 1: Schematic of small scale laboratory batch pyrolysis unit situated at UKBRC, The University of Edinburgh.

The sample in the reactor tube was heated by a 12 kW infra-red gold image furnace (P610C; ULVAC-RIKO, Yokohama, Japan) with a proportional–integral–derivative (PID) controller giving a wide range of heating rates and hold times with a maximum temperature of 1300°C. Monitoring and control of temperature in the sample bed used a thermocouple positioned 10 mm from the inner surface of the quartz tube. Nitrogen gas (N₂) was supplied to the bottom of the pyrolysis tube at a controlled rate. After preheating at the base of the reactor, the gas passes up through the sample, sweeping volatiles and syngas into a condensation system consisting of two sections. The first is heated (160±10°C); it removes entrained particulates on a filter and collects high-boiling tars in a separate trap. The second

section consists of a series of condensers and receivers where further condensable liquid products are collected (Fig. 1). Data for the main process variables, temperature, pressure and gas volume flow, are logged in real time.

Pyrolysis

Each pyrolysis experiment used a standard volume of feedstock, resulting in a different mass of material being used in runs for different feeds: 40g for pine chips, 30 g rice husk or 15 g wheat straw. In a typical pyrolysis experiment biomass was charged into the sample tube before the glassware system was assembled. The pressure sensors were zeroed and the system was purged with N₂ before establishing a steady N₂ flow rate of 0.33 L min⁻¹ as carrier gas (giving a linear cold flow velocity within the empty pyrolysis tube of approximately 3 mm s⁻¹). Samples from all feedstock types were heated at a rate of 5°C min⁻¹. For pine chip and rice husk only 100°C min⁻¹ was also used for comparison. Hold temperatures of 350°C, 450°C, 550°C and 650°C were used and maintained for 20 minutes before gradual cooling (with continued N₂ flow) until below 100°C (about 1 hr.).

After pyrolysis, product masses were determined for char and condensed liquids by weighing equipment before and after experiments. Product gas volume was measured using a volumetric flow meter (Ritter, TG5) and gas mass determined by calculation following composition analysis using a mass spectrometer (Hiden, HPR-20 QIC). Yields of each product (syngas, condensable and char) were calculated as a proportion of the mass of dry feed. Char product was removed from the pyrolysis tube and retained for analysis. Condensed liquid products comprising heavy tar and lighter oil fractions were collected and stored in a refrigerator. Gas products were disposed of by venting after composition analysis and volume measurement.

Analysis of biochar

Char samples were analysed by proximate analysis, ultimate analysis and oxidation. Prior to analysis all samples were milled to a homogenous fine powder using a ball mill (MM200; Retsch, Castleford, UK) and dried overnight at 105°C as standard practice prior to shipment of samples for analysis. Proximate analysis of all biochar samples and corresponding feedstock was carried out using thermal gravimetric analysis (TGA/DSC 1; Mettler-Toledo, Leicester, UK). Due to the small amount (mg) needed for TGA analysis moisture can be rapidly absorbed by the sample during transport and handling prior to analysis. Samples were first heated for 10 min at 105°C under N₂ to determine moisture content; the temperature was then raised at 25°C min⁻¹ to 900°C where it remained for a further 10 min to eliminate volatile matter. With air introduced to the system the sample is finally combusted (also at 900°C) for 15 minutes in order to determine ash. Fixed C is calculated on a weight per cent basis by subtracting moisture, volatile and ash values from the original mass. Elemental (ultimate) analysis of C, H and N was conducted in duplicate using an elemental analyser (Flash 2000, CE Elantech Inc, New Jersey, USA) by London Metropolitan University (London, UK). The O content was determined by difference.

The Edinburgh stability tool, used in this study, has been developed by A. Cross and S.P. Sohi at the UK Biochar research Centre, Edinburgh (Cross & Sohi 2012). Direct oxidation was conducted at the University of Edinburgh by A. Cross and K. Crombie. This stability assay forms part of a set of laboratory methods intended to provide a comprehensive set of functional assays for biochar. Briefly, biochar containing 0.1 g C is milled to a fine powder to remove any potential effect of physical structure and is treated in a test tube with 7 ml of 5% H₂O₂, initially at room temperature and then at 80°C for 48 hr. during which time the reaction is completed and the sample dried. Stable C is expressed as the percentage of the

initial 0.1g C that remains after oxidation, assessed from the gravimetric mass loss and determinations of C content before and after oxidation (Cross & Sohi 2012)

Statistical Analysis

Correlations between analytical measures of biochar stability as well as analysis of variance (ANOVA) were performed using Minitab 16 statistical software. The ANOVA statistical test was applied through a general linear model and significance of results were calculated using Tukey's HSD (Honestly Significant Difference) at a significance level of $P < 0.05$ for all materials and production conditions. Labelling systems exist to attempt to categorize R values by considering correlation coefficients ≤ 0.35 to represent low or weak correlations, 0.36 to 0.67 to be moderate correlations, 0.68 to 1.00 strong or high correlations and ≥ 0.9 to be a very high correlation (Taylor 1990).

Results and Discussion

Product Yield Distributions

The yields of char, liquid and gas obtained from each pyrolysis experiment are shown in Fig. 2 a, b, c.

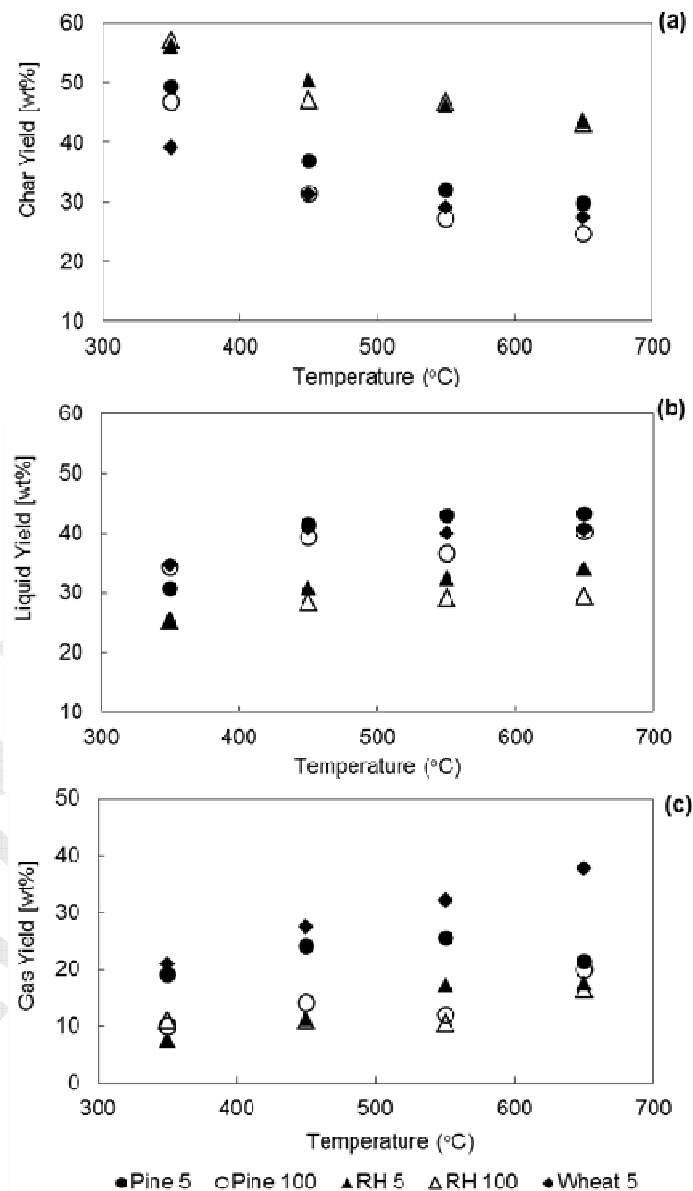


Fig. 2: Effect of production temperature on the product distribution yield for (a) char (b) liquids (c) gases present on a dry feed weight basis.

For each feedstock, higher pyrolysis temperatures resulted in a lower char yield, as expected (Antal & Grønli 2003). The distribution of product char, liquid and gas was heavily dependent on the original composition of biomass prior to pyrolysis. The cellulose, hemicellulose and lignin fractions can vary greatly between feedstock materials and these differences potentially result in contrasting product yields from pyrolysis and also the properties of those products (Vassilev *et al.* 2010). The lower biochar yields given at higher temperatures are a result of greater decomposition of organic material at higher temperatures promoting the release of volatile material. Differences in volatile material yields over the temperature range can be a result of the degree of breakdown of cellulose, hemicellulose and lignin (Demirbas 1994, 2002; Mohan *et al.* 2006; Enders *et al.* 2012). Rice husk samples yielded the largest mass of char, but conserved mass included high concentrations of inorganics present in the feedstock known from literature to be high in silica (Kalapathy *et al.* 2000). Increased char devolatilisation at higher temperature then results in a higher percentage of liquid and gaseous products (Fig. 2b,c). The differences in yields with production conditions could have an impact on the energy distribution between the char, liquid and gas products. In addition to biochar properties the distribution of the pyrolysis products should be considered when selecting production conditions, since their quality and quantity will determine their end use and so the overall impact of the system (Shackley *et al.* 2011).

Direct Oxidation (Edinburgh stability tool)

Stable C (biochar wt%), determined by the direct oxidation method (Cross & Sohi 2012), increased with pyrolysis temperature, for each feedstock (Fig. 3a).

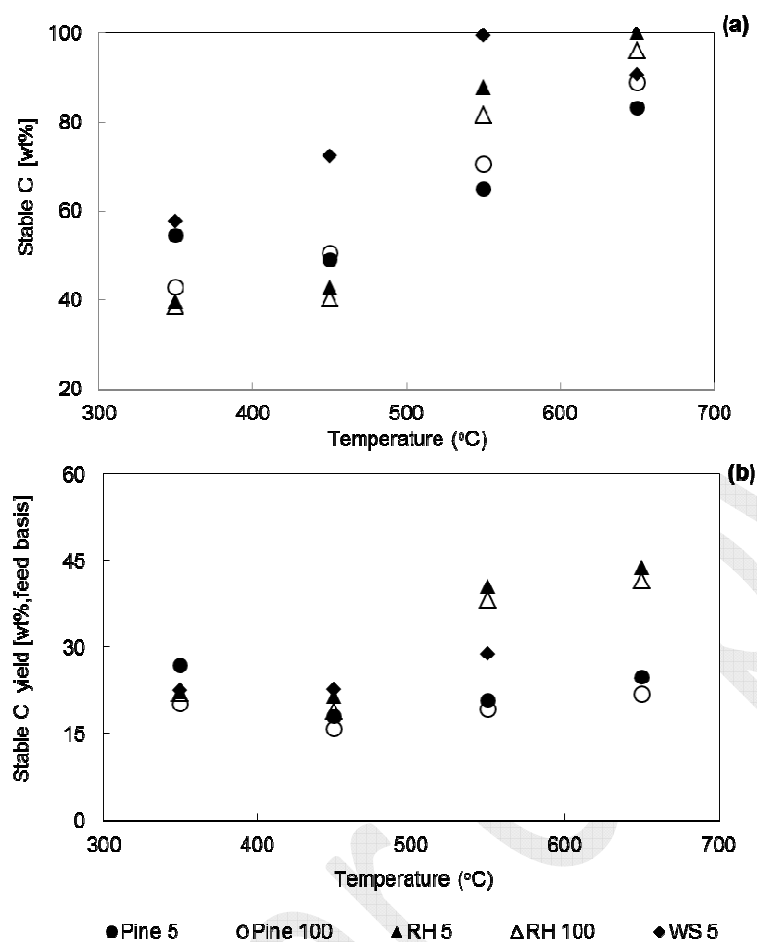


Fig. 3: Effect of increasing production temperature on the (a) Stable C and (b) Stable C yield of biochar samples. Error bars were added to the graph to show standard error of Stable C% but are not visible due to the scale of the data (n=3)

Biochar produced from wheat straw contained the highest concentration of stable C at temperatures $< 650^{\circ}\text{C}$ however analysis of wheat straw biochar produced $> 650^{\circ}\text{C}$ exhibited a decrease in stable C. The higher stable C concentration at 550°C could be attributed to the heterogeneous nature of the wheat straw used for that experimental run resulting in an increased proportion of stable C present in the feedstock. Expressing results on a feedstock weight basis removes the direct effect of (conserved) feedstock ash content, although ash may still have influenced the product yields and biochar stability indirectly during the pyrolysis

process (Fig. 3b). This measure provides an index for the efficiency of conversion of feedstock C to stable C, rather than simply how much of the C in a particular biochar is stable.

In contrast to the yield of biochar from pyrolysis, there was only a minor effect on stable C yield created in the pyrolysis of pine chips or wheat straw in the 350–650°C range of pyrolysis temperature. Despite this small variation for wheat (22.6 – 28.9 %) and pine (22.0 – 24.8 %) derived biochar, the stable C yield for rice husk samples increased from 21.6 – 40.6 % points when pyrolysis occurred at temperatures above 450°C. This observation could be a result of the high ash content typical for rice husk.

Heating rate, across the wide range of 1 to 100°C min⁻¹ investigated, did not seem to have a notable impact on the concentration of stable C in biochar although a trend showing slightly lower stable C yields in samples created at high heating rate could be discerned (reflecting lower char yields at higher heating rate). Lower variation in the yield of stable C with increasing pyrolysis temperature is of particular importance to the economic and environmental case for biochar production. Establishing how pyrolysis–biochar systems can be optimised for product that best enhances soil fertility and sequesters C, while also providing energy capture has been a key question. If the yield of stable C remains largely unaffected with increasing temperatures then biochar production could be tuned to maximise energy as well as other physiochemical properties while maintaining the C sequestration potential. The utility of high temperature biochar for soil fertility must then be considered.

Proximate Analysis

Results of proximate analysis are presented in Table 2. The ash concentration of biochar samples were influenced mainly by feedstock ($P < 0.0001$) and to a lesser extent by pyrolysis temperature ($P = 0.003$) with ash content increasing with temperature from wheat

straw and rice husk biochar (up to 20% and 50% respectively) but not for biochar from pine (<5%). In contrast to ash, fixed C and volatile matter on a dry ash free basis depended greatly on temperature ($P < 0.0001$) with no influence from feedstock ($P = 0.11$). When ash content was taken into account, however, feedstock had a significant effect ($P < 0.0001$). A strong negative correlation between ash and fixed C ($R^2 = -0.808$, $P < 0.0001$) can be used to reflect why all biochar samples produced from low ash pine contained high levels of fixed C whereas high ash rice husk biochar exhibited low volatiles and fixed C concentrations. The effect of ash on fixed C content produces a possible limitation of using proximate analysis for the determination of a stable fraction. This is due to the decreasing measured weight of ash leading to inflated values for fixed C determined via subtraction. The loss in weight associated with ash content can be due to volatilisation of ash species such as phosphorous and magnesium during thermal treatment leading to problems of fouling, corrosion and slagging and. (Ali *et al.* 1988; Darvell *et al.* 2005, Sonoyama *et al.* 2006).

The fixed C content of biochar increased with pyrolysis temperature due to increasing concentrations of volatile matter being released. Samples produced from pine feedstock showed the highest concentration of volatile matter, as well as the largest decrease (from 55.4% to 14.8%) as temperature increased from 350 to 650°C.

Expressed on a feedstock basis the yield of fixed C increased up to 450°C but not at higher temperatures (Fig. 4a).

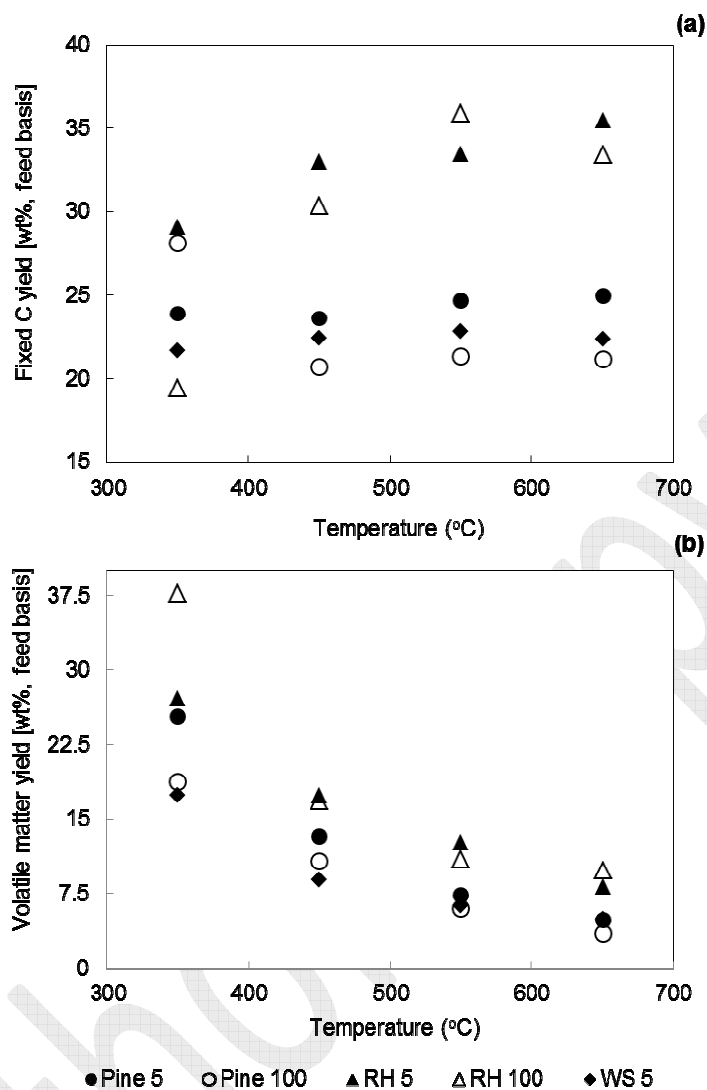


Fig. 4: Influence of temperature on the (a) fixed C yield and (b) volatile matter yield of biochar samples produced from pine, rice husk and wheat straw

This confirmed the observations of others (Antal & Gronil 2003; Mašek *et al.* 2011) and suggested that certain functional properties enhanced at higher temperature could be acquired without diminishing C sequestration. As volatile matter follows the reverse pattern to fixed C (Fig. 4b), higher temperature pyrolysis might minimise the biochar fraction susceptible to decay in soil while increasing by-products for heat and energy generation. Since small fractions of volatile matter could prove either beneficial (Elad *et al.* 2010; Graber

et al. 2010) or detrimental (Jones *et al.* 2011) to different microbial communities in soil, the composition and ideal amount of volatile matter might need to be researched and quantified. During proximate analysis the biochar sample is exposed to high analytical temperatures which when compared to environment soil conditions can be considered to be extreme therefore minimising the determined stability of carbon. Despite the term, “fixed C” is calculated by weight difference rather than quantification of elemental C and will contain other species of high thermal stability. This combined with the release of volatiles and alkali metals (P, K, As, Se, Hg etc) from the ash phase can lead to an inaccurate determination of C derived from proximate analysis that could be deemed environmentally stable.

Table 2: Proximate analysis data for biochar samples produced from selected feedstock at four temperatures (350, 450, 550 and 650°C) and two heating rates (5 and 100°C min⁻¹)

| Proximate analysis * | | | | |
|----------------------|-----------|-------------------|-------|---------|
| Sample | Fixed C % | Volatile Matter % | Ash % | Total % |
| Pine 350-5 | 47.8 | 50.8 | 1.4 | 100 |
| Pine 450-5 | 62.2 | 34.9 | 2.9 | 100 |
| Pine 550-5 | 73.9 | 22.0 | 4.2 | 100.1 |
| Pine 650-5 | 78.9 | 15.2 | 5.9 | 100 |
| Pine 350-100 | 58.0 | 38.7 | 3.4 | 100.1 |
| Pine 450-100 | 63.6 | 33.0 | 3.4 | 100 |
| Pine 550-100 | 77.7 | 21.6 | 0.7 | 100 |
| Pine 650-100 | 81.6 | 13.4 | 5.0 | 100 |
| RH 350-5 | 32.4 | 30.3 | 37.3 | 100 |
| RH 450-5 | 36.4 | 19.1 | 44.5 | 100 |
| RH 550-5 | 38.5 | 14.6 | 46.9 | 100 |
| RH 650-5 | 40.5 | 9.3 | 50.3 | 100.1 |
| RH 350-100 | 39.3 | 20.7 | 40.1 | 100.1 |
| RH 450-100 | 35.0 | 19.4 | 45.6 | 100 |
| RH 550-100 | 37.0 | 11.3 | 51.7 | 100 |
| RH 650-100 | 38.6 | 11.3 | 50.0 | 99.9 |
| WS 350-5 | 49.5 | 39.6 | 10.9 | 100 |
| WS 450-5 | 59.2 | 23.2 | 17.6 | 100 |
| WS 550-5 | 62.8 | 17.2 | 20.0 | 100 |
| WS 650-5 | 64.4 | 14.2 | 21.3 | 99.9 |

*, Moisture free basis

Ultimate Analysis

Results for all biochar samples are shown in Table 3. Statistical analysis indicated that temperature ($P < 0.0001$) was the main determinant of CHNO results expressed on a dry ash free basis. However, similar to proximate analysis, when the ash concentration was not included in the CHNO results, the impact of feedstock increased ($P = 0.547$, $P = 0.001$) to

becoming equally important as pyrolysis temperature. For biochar from each feedstock, biochar C content increased with pyrolysis temperature (and inversely to biochar yield) through preferential elimination of N, H and O in volatile matter. Loss of O and H can be attributed to the scission of weaker bonds within the char structure such as alky-aryl ether bonds and the formation of more resistant structures (Demirbas 2004). Total C content for all biochar samples were considerably greater than the total C of their respective biomass. However, when biochar yield was taken into account and total C expressed on a feedstock weight basis it was found (Fig. S1) to be largely independent of pyrolysis temperature (as with fixed and stable C yields).

The effect of elemental composition on the molar ratios O:C and H:C was assessed (Fig. S2). All biochar samples had lower H:C and O:C ratio than their parent biomass owing to preferential elimination of O and H relative to C in volatile matter. Due to the use of molar ratios, small changes in H content had a proportionally larger effect on H:C than the respective changes in O. Both ratios decreased in biochar with increasing pyrolysis temperature. The ratio of H:C at each temperature decreased in the order WS > RH > P, implying that pine feedstock yielded biochar of the highest stability – a alternative outcome to that obtained from O:C and stable C analysis.

Van Krevelen diagrams plot H:C against O:C to provide clear, visual indication for the origin and maturity of petroleum and coal and more recently applied to biochar to demonstrate the evolution of composition with temperature (Hammes *et al.* 2006; Preston & Schmidt 2006). In Fig. 5, samples from the current work are identified by feedstock and grouped graphically by pyrolysis temperature.

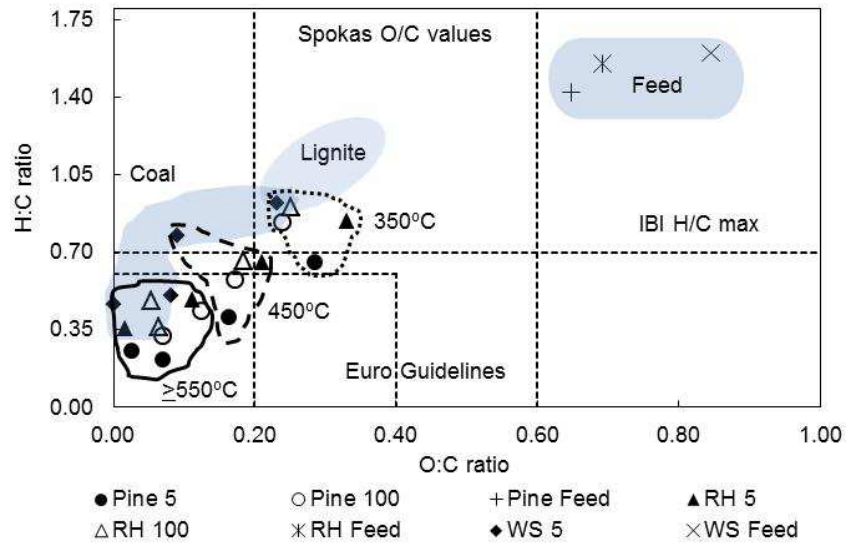


Fig. 5: Van Krevelen diagram comparing the O:C and H:C ratios of biochar samples with guidelines obtained from literature.

Biochar samples residing furthest to the right on the O:C scale were produced at 350°C, with those created at higher temperature grouped progressively closer to the origin. Results for additional materials in the literature have been added to Fig. 6, to indicate how the present samples compare to coal and lignite (Hammes *et al.* 2006; Van der Stelt *et al.* 2011) as well as the regions of stability defined by Spokas (2010) and classification guidelines for biochar (IBI Guidelines 2012; Schmidt *et al.* 2012).

Table 3: Ultimate analysis of C, H, N and O for all biochar samples and corresponding O:C and H:C ratios

| Ultimate analysis † | | | | | | |
|---------------------|-------|------|------|-------|------------------|------------------|
| Sample | C% | H% | N% | O%* | O:C atomic ratio | H:C atomic ratio |
| Pine 350-5 | 69.64 | 3.79 | 0.00 | 26.58 | 0.29 | 0.65 |
| Pine 450-5 | 79.86 | 2.68 | 0.00 | 17.47 | 0.16 | 0.40 |
| Pine 550-5 | 89.93 | 1.57 | 0.00 | 8.50 | 0.07 | 0.21 |
| Pine 650-5 | 94.61 | 1.97 | 0.00 | 3.42 | 0.03 | 0.25 |
| Pine 350-100 | 70.97 | 4.94 | 1.37 | 22.73 | 0.24 | 0.83 |
| Pine 450-100 | 77.34 | 3.72 | 1.01 | 17.93 | 0.17 | 0.57 |
| Pine 550-100 | 82.32 | 2.96 | 0.84 | 13.88 | 0.13 | 0.43 |
| Pine 650-100 | 87.89 | 2.35 | 1.47 | 8.29 | 0.07 | 0.32 |
| RH 350-5 | 66.14 | 4.67 | 0.00 | 29.19 | 0.33 | 0.84 |
| RH 450-5 | 74.93 | 4.11 | 0.00 | 20.97 | 0.21 | 0.65 |
| RH 550-5 | 84.03 | 3.43 | 0.00 | 12.54 | 0.11 | 0.49 |
| RH 650-5 | 95.13 | 2.85 | 0.00 | 2.02 | 0.02 | 0.36 |
| RH 350-100 | 70.87 | 5.36 | 0.00 | 23.77 | 0.25 | 0.90 |
| RH 450-100 | 76.86 | 4.26 | 0.00 | 18.88 | 0.18 | 0.66 |
| RH 550-100 | 89.98 | 3.61 | 0.00 | 6.40 | 0.05 | 0.48 |
| RH 650-100 | 89.61 | 2.74 | 0.00 | 7.64 | 0.06 | 0.36 |
| WS 350-5 | 70.88 | 5.46 | 1.71 | 21.96 | 0.31 | 0.92 |
| WS 450-5 | 83.11 | 5.40 | 1.36 | 10.12 | 0.12 | 0.77 |
| WS 550-5 | 86.21 | 3.63 | 0.81 | 9.36 | 0.11 | 0.50 |
| WS 650-5 | 94.90 | 3.68 | 1.53 | 0.00 | 0.00 | 0.46 |

*, determined by difference

† Dry ash free basis

Comparison of stability determination

Individually, five approaches to comparing the stability of biochar suggested increasing biochar stability with higher pyrolysis temperature: increases in stable C, fixed C content and a decrease in volatile matter, O:C and H:C. To assess relationships between the different analytical techniques for stability, the results were plotted against each other in correlation diagrams and presented in Fig. 6 with accompanying correlation coefficient R values. As stable C determined by the Edinburgh stability tool is calculated on a dry ash free basis the results for fixed C, volatile matter and elemental ratios were also converted to a dry ash free basis to minimise variability of ash content between feedstock types. Heating rate was found to have no statistical effect ($P > 0.5$) on fixed C, volatile matter, stable C and O:C ratio however significant effect was observed for feedstock on H:C ratio ($P = 0.007$).

The results from direct oxidation were correlated with H:C and O:C for each individual feedstock as well as a total correlation of all the data. In most cases the correlations were considered to be very strong for all feedstock at both heating rates. Strong correlation between stability indicators for samples produced for the same feedstock does not confirm compatibility between methods for more diverse samples from multiple types of biomass. The differing gradient of correlation coefficients between the feedstock and therefore overall scatter of data points should also be considered when reviewing the compatibility between analytical methods for determining stability.

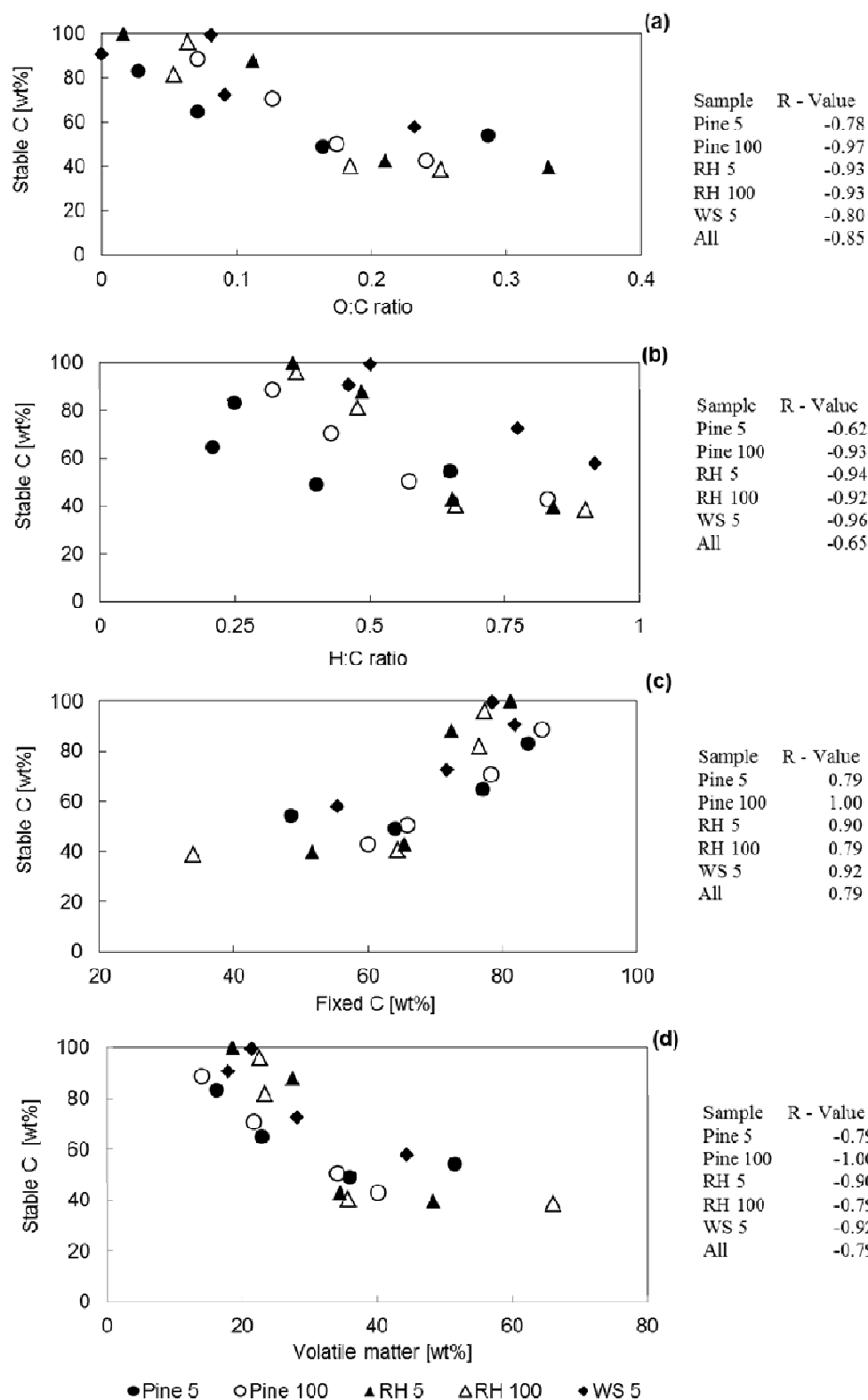


Fig. 6: Comparison of results between the Edinburgh stability data and alternative methods for biochar stability: proximate and elemental analysis, (a) Stable C vs O:C ratio (b) Stable C vs H:C ratio (c) Stable C vs fixed C (d) Stable C vs volatile matter

When comparing the correlation of stable C vs O:C/H:C for all samples (Fig. 6a,b), increased scatter of the H:C values resulted in lower correlation coefficients ($R = -0.645$, $P = 0.002$) compared to that for O:C ($R = -0.847$, $P < 0.0001$). This large scatter could be due to the trend previously mentioned (Fig. S2b), where at any of the selected production conditions the H:C ratio follows a decreasing trend of $WS > RH > P$. This observed trend indicates that the variation in H:C ratio could be influenced to a greater extent by feedstock properties compared to that of O:C, confirmed by the higher statistical dependency of H:C ($P < 0.0001$) than O:C ($P = 0.064$). The strong influence of feedstock on H:C ratio is derived from the enhanced impact of feedstock on H concentration ($P < 0.0001$, dry ash free basis) whereas O content is not influenced by feedstock ($P = 0.075$). As seen in Table 3 biochar samples produced from pine and rice husk under the same production conditions contain similar concentrations of C which also applies to wheat straw biochar produced at higher temperatures ($\geq 550^\circ\text{C}$). The decreasing trend ($WS > RH > P$) of H content present in the biochar samples therefore resulted in higher H:C ratios. The absent effect of feedstock on O content could stem from its determination based on subtraction rather than analytical measurement of the O concentration. This approach can lead to inaccuracy in the quantification of O due to assumptions made over the composition of biochar. Therefore O derived data can influence the correlation with other measures of stability while failing to demonstrate the significance of external factors such as feedstock.

Strong correlation was observed when comparing direct oxidation with fixed C (Fig. 6c) or volatile matter (Fig. 6d) for each feedstock and heating rates ($R = 0.793$, $P < 0.0001$). Identical R values were observed for both graphs demonstrating the relationship between decreasing volatile matter and the resulting increase in fixed C concentration. The overall spread of data within both graphs is potentially due to the influence of the varying ash concentration of high (RH), medium (WS) and low (P) present in the char samples as well as

any impact of heterogeneous feedstock samples. The correlation between the varying methods could be influenced by the volatilisation of ash components during proximate analysis.

Correlations between the more established analytical methods for stability indication of fixed C vs O:C, fixed C vs H:C, volatile matter vs O:C and volatile matter vs H:C were carried out and shown in Fig. S3. Strong correlations were again demonstrated for each feedstock at both heating rates as well as the total correlation of the whole data set ($R \geq 0.93$). Overall correlation values were representative of weaker correlation when comparing proximate data against H:C ($R = -0.806$, $P < 0.0001$) rather than against O:C ($R = -0.888$, $P < 0.0001$) however both correlations were determined to be strong. Increased scatter can be seen in graphs comparing fixed C/volatile matter with H:C ratio, similar to that shown in Fig. 6b, although not to as great an extent, demonstrating the larger spread in H:C for all biochar samples reiterating the impact of feedstock on H:C determination and therefore it's correlation with proximate analysis data.

Samples for which divergence is observed between methods or where the scatter in the relationship is enhanced can provide clues for revealing the strength, mode and susceptibilities of each method to external influences and therefore evaluate the comparison to soil conditions when biochar will ultimately degrade.

Conclusion

A new method of direct chemical oxidation of biochar, alongside three candidate methods for determination of relative biochar stability, i.e. fixed carbon content, O:C and H:C ratios, was applied to a systematic set of biochar samples to indicate their relative stability. The results showed that temperature had the strongest effect on stability of biochar, with stability increasing with maximum treatment temperature (at constant residence time at peak temperature). However the yield of stable C, fixed C and total C were found to be independent of temperature for biochar prepared from low ash feedstock (pine and wheat straw). On the other hand the stable C yield of biochar produced from high ash biomass (rice husk) was seen to increase above 450°C creating two levels for stable C yield between 350-450°C and 550-650°C. Therefore increasing pyrolysis temperature could be utilised to optimise additional benefits such as structural, chemical and energy generation without sacrificing the C sequestration potential.

Comparison of results from direct oxidation of biochar with stability indicators derived from proximate and ultimate analysis showed a strong correlation between the approaches across feedstock and production conditions (pyrolysis temperature and heating rate). However, despite the strong correlations, there was a sufficient degree of scatter, as well as indication of different sensitivities to feedstock properties, that would reduce practical usability of these correlations for predictive purposes. The results of this paper aim to highlight the sensitivity of the current methods for stability assessment while proving valuable in defining protocols for defining stability or developing new improved methods.

The analysis of a systematic set of biochar samples generated using a small scale batch pyrolysis unit capable of accurately replicating production conditions allowed for the detailed investigation of varying biochar properties with experimental conditions. However the reproducibility of these results and therefore technique correlation could quite possibly

478 vary greatly depending on pyrolysis unit as well as scale of production. Therefore the
479 collection and analysis of samples from various pyrolysis units on differing scales using a
480 variety of production conditions would utilise a wider range of variables which can then be
481 statistically analysed for significance to biochar properties and used as calibration to improve
482 the prediction of biochar stability in soil.

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Supplementary Material

Carbon Yield results

As temperature is increased the concentration of C in biochar also increases. However, this is not the case for char yield is taken into consideration. By representing the total C on a feedstock weight basis there is little variation over the temperature range 350°C-650°C as shown in Fig. S1.

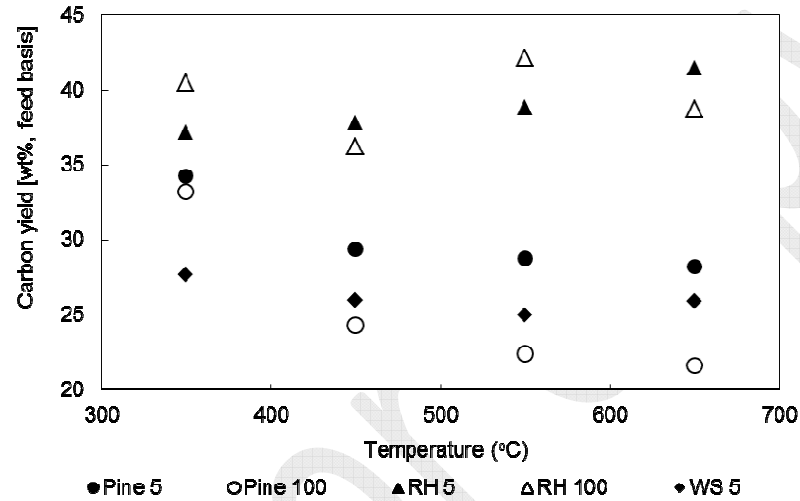


Fig. S1: Variation of C yield with increasing production temperature. Error bars were added to the graph to show standard error of C% analysis but are not visible due to the scale of the data (n=2)

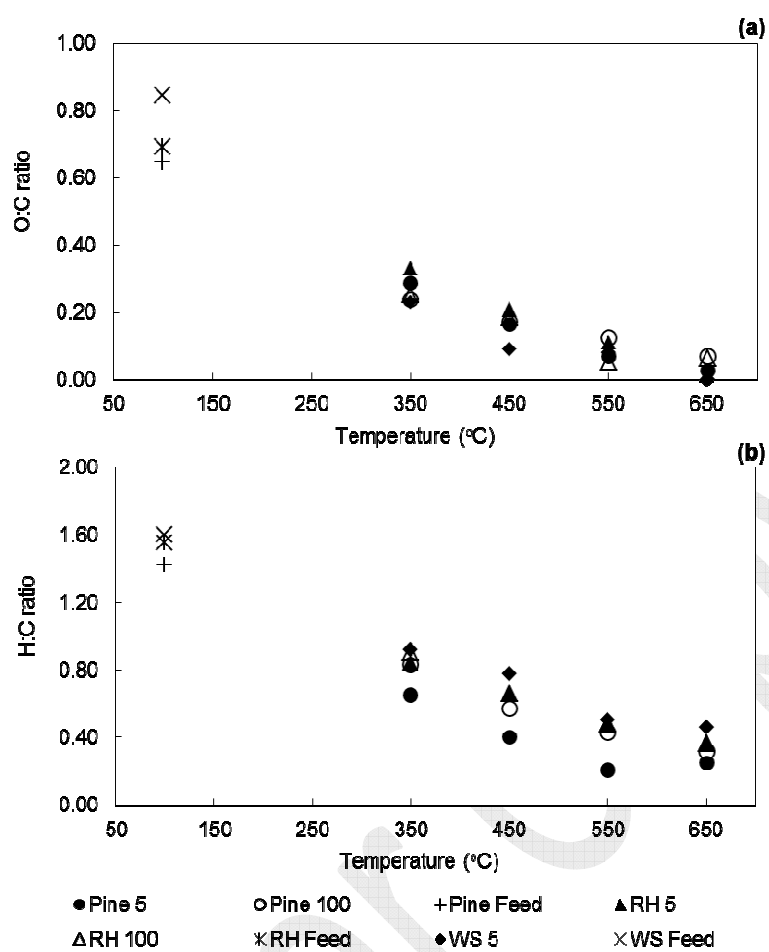
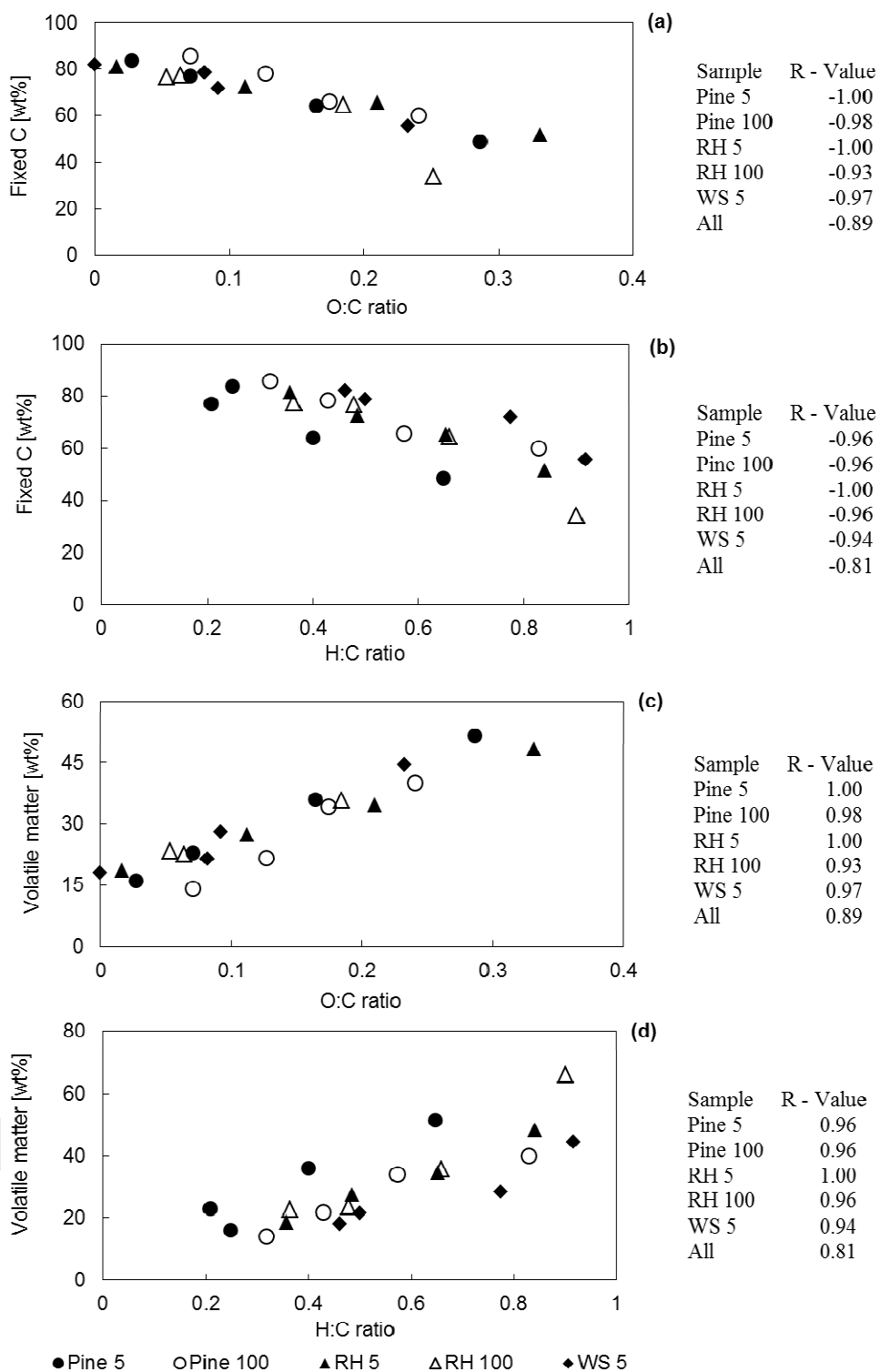


Fig. S2: Influence of temperature on the (a) O:C ratio and (b) H:C ratio of biochar samples and parent biomass

612 *Correlation between Proximate and Elemental analysis*

613 The results obtain from proximate analysis were compared to those produced by
614 elemental analysis to investigate the correlation between two different methods for stability
615 determination. The correlation between techniques and accompanying R values are shown in
616 Fig. S3

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617

618 Fig. S3: Comparisons between proximate and elemental analysis data to show correlations

619 between (a) fixed C vs O:C ratio (b) fixed C vs H:C ratio (c) volatile matter vs O:C ratio (d)

620 volatile matter vs H:C ratio

621